

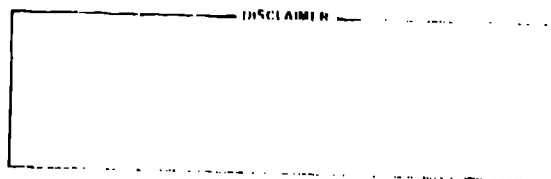
TITLE: SOLAR-THERMAL HYDROGEN PRODUCTION

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MASTER

SUBMITTED TO: Contribution to the Proceedings of the STTFUA Workshop
on STTF Testing for Long-Term Performance, January 7-9, 1981,
Albuquerque, NM

University of California



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SOLAR THERMAL HYDROGEN PRODUCTION*

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ABSTRACT

Since hydrogen is not only an eventual and attractive fuel but is also a prime intermediate in the production of many fuels and chemicals, one extremely valuable utilization of a solar thermal facility would be its operation as a system for hydrogen production. Such a use would also fulfill the important requirement for energy storage.

Solar thermal systems appear to offer the only practical method for significant hydrogen production from solar energy. The production could utilize advanced methods of water electrolysis if highly efficient generation of solar electricity were developed. Thermochemical cycles for water decomposition appear to be more promising if cycles that match the characteristics of solar heat sources can be developed. Advanced cycles based on solid sulfate or solid oxide decomposition reactions should interface advantageously with solar thermal systems. Sulfuric acid cycles can serve as standards of comparison for these new cycles as they are discovered and developed.

*This document is prepared for the Office of Solar Energy, U.S. Department of Energy.

I. INTRODUCTION

In a consideration of the long-term utilization of solar thermal systems, it is apparent that the production of fuels will be one of the major applications. This is to be expected not only because of the eventual need of non-fossil fuels, but also because fuels can be stored and the practical use of high-temperature solar heat will require the development of processes that exhibit high conversion efficiencies and that also incorporate energy storage. Since hydrogen can fulfill the requirement for energy storage, is itself an attractive transportable fuel and is the "prime intermediate" in the production of many fuels and chemicals, a reasonable fraction of the effort in STTF testing should be directed toward the eventual development of efficient processes for the production of hydrogen from water.

The potential advantage of hydrogen as an energy carrier and as a fuel have been emphasized many times and over the past few years increasing attention has been given to solar energy for producing hydrogen. A great deal of research has been and is concerned with the possible use of solar radiation for the photochemical or "photocatalytic" decomposition of water. When viewed as studies of fundamental phenomena, these research programs are very interesting and should not be discouraged. However, from the perspective of process development (even long range) the following realities should be recognized:

The decomposition of water is a high energy process and only a small fraction of the sunlight is at wavelengths with sufficient energy for the reaction.

Sunlight is a diffuse energy source. Consequently, the cost per unit area of the material or system that intercepts the sunlight will be an important part of the overall system cost (e.g. a concentrating mirror, a chemical solution or a semiconductor).

Eventually, hydrogen must be produced in high volume at low cost in order to be an important part of the future energy economy.

It seems reasonable to suggest that solar-based photochemical processes have realistic prospects for practicality only if the primary quantum step does not require excessive energy and in addition only if the product is more valuable than hydrogen and cannot conveniently be

produced by a solar thermal method. Certainly, thermal systems appear to offer the only practical probability for significant hydrogen production from solar energy.

II. PRODUCTION TECHNIQUES

A. Electrochemical Hydrogen Production.

The electrolysis of water is a well-known technique and although present electrolyzers are relatively inefficient, a worldwide effort is underway to develop advanced electrolysis methods for alkaline solutions, acidic solutions or for the high-temperature electrolysis of steam by the use of an ion conducting ceramic as an electrolyte. At present, nine countries are participants in I.E.A. programs to develop these techniques.* Excellent progress is being made and it is probably not overoptimistic to project the eventual availability of electrolyzers with voltage efficiencies of 85-90%. Consequently, if systems for the efficient production of solar electricity can be developed, economic solar-electric hydrogen production may become feasible. Certainly, this combined system would assist in solving the energy storage problem that must be solved if solar-electric is to become a significant factor in the future energy economy.

At the present time, solar thermal programs for electricity are directed primarily toward coupling existing steam-electric or Brayton cycle technology to the different solar thermal systems that are under development. The approach is practical and permits focusing most of the available effort on the crucial problems of developing the heat sources themselves. However, it is probable that existing power production methods will not yield the efficiencies potentially available from the high temperature solar sources when these have been fully developed. Therefore, it seems prudent to devote some effort to developing alternate, more efficient power conversion processes. It is in this area (e.g. topping cycles or even direct conversion) where STTF testing might evaluate concepts that can lead eventually to higher conversion efficiencies.

It should be noted that solar photovoltaic systems can be used to power electrolysis cells for hydrogen production. It is obvious that there will be many special situations where small systems will be useful. However, 1

*Papers representative of the different methods are listed as references 1, 2 and 3.

realistic appraisal it should be apparent that solar thermal systems are inherently more efficient by about a factor of three and are probably more economical by a larger factor. Therefore, any large volume solar hydrogen production will require the development of solar thermal systems.

B. Thermochemical Hydrogen Production.

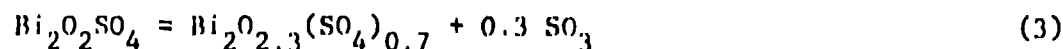
It is widely recognized that for high temperature heat sources, production processes based on thermochemical cycles can yield higher efficiencies than an overall path where heat is converted to electricity and water is decomposed electrochemically. Consequently, there is a worldwide effort to develop cycles to exploit the potential of thermochemical water splitting. It should be noted that the total effort is small in comparison to the effort considered necessary to develop a new technology. In addition, most of the programmatic support has been given to applied programs concerned with early selection and engineering design of a specific cycle rather than studies which might lead to the identification of better cycles. Nevertheless, several thermochemical cycles have been shown to be technically feasible and three H_2SO_4 based cycles (ref. 4, 5, and 6) are at a bench-scale level of development. The progress is encouraging, but, in principle, more efficient cycles are possible, particularly for high temperature isothermal heat sources.

For maximum efficiency, one would wish to discover and develop cycles that approximately fulfill the criteria for an "ideal" cycle for the temperature available from each heat source. These criteria have been described previously (ref. 7) and will not be repeated here except to note that large entropy changes for the high temperature endothermic step will permit a lower maximum temperature and also minimize the number of reaction steps required for the thermochemical cycle. Sulfate decomposition reactions are examples of large entropy processes and H_2SO_4 decomposition is a special example of sulfate decomposition. However, for each of the sulfuric acid cycles referenced above, the acid is produced in aqueous solution and the concentration of the solution is an energy intensive step. After "drying," $\text{H}_2\text{SO}_4(\ell)$ is vaporized to form $\text{H}_2\text{SO}_4(\text{g})$ at $\sim 700\text{K}$ (depending on system pressure). This step requires about 40% of the total energy needed for the decomposition of $\text{H}_2\text{SO}_4(\ell)$. With increasing temperature the $\text{H}_2\text{SO}_4(\text{g})$ decomposes to $\text{H}_2\text{O}(\text{g})$ and $\text{SO}_3(\text{g})$ and the $\text{SO}_3(\text{g})$ then decomposes to $\text{SO}_2(\text{g})$ and

$O_2(g)$. For high yield in this last step, a temperature near 1300 K is required. Consequently, the overall process of sulfuric acid decomposition requires heat over a wide temperature range and is reasonably well matched with the heat delivery characteristic of a cooling gas stream, e. g. from a circulating gas-cooled reactor. Of course, an isothermal heat source can be used for sulfuric acid cycles, but (in an ideal sense) with a loss of potential efficiency in comparison with cycles based on solids decompositions which can match the isothermal, high-temperature heat available from solar thermal systems.

Several laboratories have considered the formation of a metal sulfate from the reaction of H_2SO_4 in solution with a metal oxide (or an oxysulfate) as a means to avoid the energy intensive step of concentrating the sulfuric acid. Ideally, the sulfate should be insoluble, should not be highly hydrated and should not require excessive temperature (excessive heat) for its decomposition. The bismuth sulfate cycle (one of the sulfates under study at Los Alamos) is an example of sulfuric acid-metal sulfate cycles.

Bismuth sulfate decomposes through a series of intermediate oxysulfates rather than directly to bismuth oxide. Equations 1, 2, and 3 describe the decomposition steps that are relevant to the cycle.

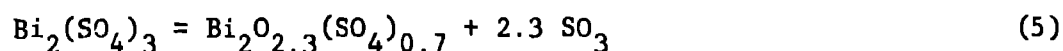
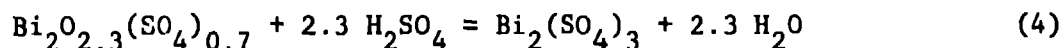


Enthalpies for reactions 1 and 2 were measured experimentally at Los Alamos (ref. 8). The values are 161 and 172 kJ/mol for reaction 1 and 2, respectively. Although the enthalpy for reaction 3 was not determined, it is expected to approximate that for reaction 2 since the decomposition proceeds rapidly to the bismuth oxysulfate product of reaction 3.

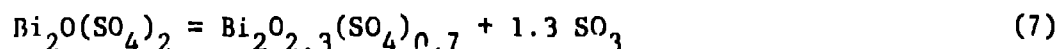
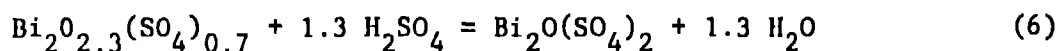
It has been found that $Bi_2O(SO_4)_2$ is the stable sulfate in contact with sulfuric acid in the concentration range of 3.0 to 52.7 wt% at ambient temperatures. This oxysulfate contains three waters of hydration. At acid concentrations higher than 52.7 wt% the stable sulfate is $Bi_2(SO_4)_3$ with no waters of hydration. From such studies it is clear that there are two alternate bismuth sulfate cycles based on an initial reaction to form sulfuric

acid. These may be described as Alternate I and Alternate II. Both cycles contain an additional step for the decomposition of SO_3 to SO_2 and O_2 .

ALTERNATE I



ALTERNATE II



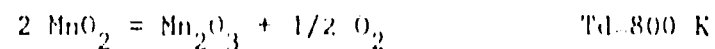
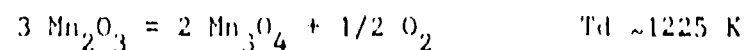
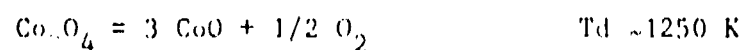
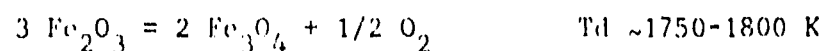
Alternate I requires higher strength sulfuric acid, but for each mole of SO_3 finally decomposed, requires a lower bismuth inventory and less energy for drying the solid sulfate. Alternate II requires lower strength sulfuric acid. Thus, its potential advantage would be in combination with the hybrid sulfuric acid cycle and depend on the possibility that significantly less energy might be required to form the dilute acid.

At this time it is not clear that sulfuric acid-metal sulfate cycles will in practice prove to be better than the sulfuric acid cycles. Whether the possible advantages are realized will depend not only on the development of satisfactory methods for handling solids, but also on improvements that may still be made on the sulfuric acid cycles themselves. Additional development will also be required before the "best" sulfate can be chosen for coupling with a sulfuric acid cycle. Finally, it should be noted that sulfate cycles are possible where the formation of sulfuric acid is not required as an intermediate step.

In addition to solid sulfate cycles as advanced alternatives to sulfuric acid cycles, it is apparent that cycles based on solid oxide decomposition as the high temperature step may offer unique advantages for cou-

pling with a solar furnace since the oxide can be heated and decomposed in air at temperatures where the oxygen dissociation pressure exceeds the pressure of oxygen in the atmosphere. Thus, the oxide could be heated directly by solar radiation entering through an "air window" and the difficult problem of transmitting heat to the process, either through a container wall or a quartz window, might be greatly simplified. The key to practicality for such cycles will be determined by the chemistry of the low temperature reactions required to form the oxide plus an intermediate that can evolve hydrogen as a product in an additional sequence of reactions. Since the decomposition of an oxide exhibits a relatively low entropy change (in comparison to sulfate decomposition) one might expect that the low temperature reactions will be reasonably complex and will probably require solution chemistry for separating the oxide from other products. However, it seems probable that the advantages of oxide cycles for solar heat may overshadow the disadvantages of the solution chemistry.

At Los Alamos, studies have been initiated to determine practical conditions for the low temperature steps in oxide cycles. Oxide decomposition reactions are also being evaluated in rotary kiln and fluidized bed systems. Specific oxides being considered for a range of decomposition temperatures are:



Initial study is on the $\text{Co}_3\text{O}_4/\text{CoO}$ pair.

It should be emphasized that conditions for the low temperature reactions must still be determined and demonstrated. The possible advantages, however, appear to offer sufficient justification for significant effort, not only at Los Alamos but also in other laboratories.

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